SYNTHESIS CHARACTERIZATION AND MULTI FUNTIONAL APPLICATION OF $Bi_2Zr_2O_7$ BASED MATERIALS

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1.0 INTRODUCTION

Nanotechnology refers to the branch of science encompasses a fabrication and application of chemical, physical, and biological systems towards designing and development of various devices by manipulating atoms and molecules at nanoscale i.e. having one or more dimensions of the order of 100 nanometres or less [1-4]. Many of the applications of nanotechnology involve new materials that have very different properties and new effects compared to the same materials made at larger sizes. This is due to the very high surface to volume ratio of nanoparticles compared to larger particles, and to effects that appear at that small scale but are not observed at larger scales [5-7]. The applications of nanotechnology can be very beneficial and have the potential to make a significant impact on society. Nanomaterials of different sizes and shapes, such as, nanowires, nanotubes, nanorods and nanocomposites are currently being investigated for their potential to revolutionize technological applications [8,9]. Nanotechnology has already been embraced by various sectors such as medicinal, material science, optics, sensors, industrial and energy engineering activities. Nanomaterials may also offer new opportunities for the reduction of environmental pollution like decontamination of waste water by photocatalytic process [10-15].

In recent years, nanotechnology has emerged as a multidisciplinary field in which gaining a fundamental understanding of the electrical, optical, magnetic, and mechanical properties of nanostructures promises to deliver the next generation of functional materials with wide-ranging applications [16-18]. In this way the nanomaterials can plays a vital role by providing excellent solutions to technological and environmental challenges in the areas of waste water treatment and electrochemical sensors activity towards various chemical/bio-chemical

substances. Photocatalytic degradation is an advanced oxidation process, which can be used to degrade pollutants with high concentration using a semiconductor photocatalysts. Semiconducting oxide photocatalysts have been increasingly focused in recent years due to their potential applications in environmental waste water treatment. Semiconductor photocatalyst has enormous potential to treat organic contaminants in waste water sample using light energy. The oxidation and hydrolysis of pollutant molecules occurs by absorption of photons in the Sun-light or Ultra-Violet (UV) radiations. The activation of semiconductor photocatalyst with light radiation leads to the migration of the photo responsive electron from the valence to the conduction band, generating photo-induced electron and hole pairs. Photo-generated electron and hole pairs react with oxygen, water and hydroxyl groups to produce reactive oxygen species. These radicals can interact with pollutant molecules, resulting in the complete degradation of pollutants in waste water [19-25].

Various semiconductors (TiO_2, ZnO, Fe_2O_3, CdS, ZnS) can act as photocatalysts but zirconia related nanomaterial has been most commonly studied due to its ability to break down organic pollutants and even achieve complete mineralization. In the past decade, zirconia (ZrO_2) has headed other oxides due to its band gap. Zirconia exists in three crystalline phases, viz., monoclinic, tetragonal and cubic. Due to its various crystalline structure, it has got diverse applications in various fields such as optoelectronic devices, photocatalytic, biomedical, catalysts, sensors, microelectronic devices, solar cells, coatings [26, 27] etc. Recently zirconia acts as an attractive candidate in the field of photocatalysis in order to remove the contaminants present in the dye and degrade it. As the band gap of ZrO_2 is ~ 5.0 eV which is suitable for the photocatalytic degradation under UV-light. There are many papers that add support for UV light irradiation and there are only few papers available for Sunlight responses of ZrO_2 photocatalyst. Among various structures of ZrO_2 nanomaterial, the spinel structure of $A_2B_2O_7$ has been studied owing to its novel efficient photocatalytic

behaviors, improved electric properties and its versatile applications in catalysis, gas sensing and supercapacitor [28, 29]. After a systematic investigation on $A_2B_2O_7$ type of material with pyrochlore structure, $Bi_2Zr_2O_7$ was chosen in this study as Bismuth (III) and Zirconium Oxides exhibit similar polymorphic reforms. In addition, a good photo response for visible light region was observed for bismuth zirconate semiconductor. Furthermore, the researchers were tempted to prepare $Bi_2Zr_2O_7$ due to the combination of less conductive stabilized ZrO_2 and high oxide ion conductivity of Bi_2O_3 [30]. It was identified that for fabricating novel nanoelectronics and optical devices, metal doped ZrO_2 was very much helpful due to its intentional defects that was generated by doping ions [31– 33]. Hence, we attempted to do research work on $Bi_2Zr_2O_7$ nanomaterial and its photocatalytic applications.

Further, nanotechnology is fast advancing into various areas such as biology, chemistry, physics and material science, demonstrating its versatility and playing a vital role in the betterment of society. The flourishing nanotechnology has a strong storage energy capacity and potential towards sensors activity to detect chemical and bio-molecule substances [34,35]. Electrochemical applications to carry out the capacitance study and sensor study were found in a wide range of commercial applications. To detect certain toxic substance by sensor method is attracted and most needed one in past decade. The simple and easy method for the analysis is by the electrochemical method in which the electrode prepared were used as sensors that detect the information allied with chemical reactions and convert it into the form of measurable current (amperometric/voltammetric method), conductivity (conductometric method), and voltage or potential (potentiometric method). Thus, an attempt to subject our aimed nanomaterial $Bi_2Zr_2O_7$ were subjected to electrochemical studies and sensors studies in our work for the first time [36-38].

The synthesis method plays an important role to improvise the physical and chemical

properties of the nanomaterials. In this regard as many methods were on research, we have opted the solution combustion method which is simple and less expensive method. The slight drawback of this method is using chemical fuel which release more toxic gases. By considering these limitations we tried to use the green fuel from leaf extract which results in less toxic material to the ecosystem.

Thus, the goal of our presented work is to synthesize heterogenous nanomaterial $Bi_2Zr_2O_7$ by combustion route by using pudina leaf extract as green fuel, with modified chemical and physical properties in particularly designed for environmental systems. Nanostructured $Bi_2Zr_2O_7$ NPs have been organized and tested as excellent catalysts for the decolorization of organic dyes RhB and MB by means of UV and Sunlight showing better photocatalytic performance than their industrial counterpart. Eventually, the effectiveness of Ag doped $Bi_2Zr_2O_7$, Fe doped $Bi_2Zr_2O_7$ and hydroxyapatite-$Bi_2Zr_2O_7$ (BZO-HA) composite has been chosen for this thesis work and as they have potential applications in various fields like photo-catalytic studies, energy storage systems, sensors activity and biological applications. Mainly in electrochemical sensor studies and dye degradation process as a photocatalyst have got more attention due to the excellent sensing activity towards chemical/bio-molecule detections and organic dye degradation under Sun-light irradiation, which can reuse many times that can benefit in both cost reduction and time consumption. From the results and discussion of our current work we could say that the work successfully achieved the synthesis of $Bi_2Zr_2O_7$ and its related compounds with its enhanced applications.

2.0 PROBLEM STATEMENT

Contamination of drinking water, dye, pharmaceutical waste, and heavy metal leaching into water bodies, as well as disruption and eutrophication of water bodies, are the difficulties linked with persistent pollution. To treat wastewater contaminants, many techniques have

been developed. Filtration, flocculation, coagulation, biological treatment, absorption/adsorption, sedimentation, physical and chemical treatment, and membrane process, are all examples of these processes. Unfortunately, these treatment techniques are ineffective at removing organic pollutants and heavy metals from wastewater. Aside from being chemically and operationally demanding, the processes necessitate huge systems, infrastructure, and engineering skills, making them cumbersome, ineffectual, slow, and expensive. The simplicity of maintenance and inexpensive cost of this system is its key advantages. On the other hand, this method is not appropriate for the removal of heavy metals and low biodegradable contaminants. One drawback of several of these methods is the requirement for meticulous monitoring and regular cleanup of chemical sludge and residue. [39,40]

Photocatalysis has emerged globally as a sustainable solution for wastewater treatment due to rapid advances in the development of novel nano-photocatalysts. It has been suggested as a potential method for wastewater treatment since it is effective, non-selective, as well as efficient, and the photocatalyst may be reused multiple times. This method allows for the removal of a wide range of contaminants while also aiding in the mineralization or breakdown of complex contaminants such as landfill leachate into less complicated substances like water, carbon dioxide, and inorganic ions [41]. As a result, photocatalysis has been identified as one of the efficient methods for the mineralization of complex contaminants as a viable alternative technology capable of degrading and eliminating complex pollutants [42].

Semiconductor photocatalyst has been considered to be a promising pathway for solving water pollution problems by decomposing pollutants and disinfection. Activation of the semiconductor photocatalyst through the absorption of a photon of ultra-band gap energy

creates electron–hole pairs, electrons in the conduction band (CB) and holes in the valence band (VB). Then the reactive oxygen species, such as hydroxyl radical, superoxide radical and H_2O_2, will be yielded through a series of reactions, which can mineralize the organic contaminants.

Dramatic increase of the interest towards the use of nanomaterials like TiO_2, ZnO, MgO, CuO and their composites in photocatalysis for energy crisis, bacterial infection and environmental pollution was observed since the discovery of TiO_2. But the utilization of nature available solar energy for the process became a thoughtful process now. Intending to make them available for practical applications, massive effort has been made by researchers to explore the factors related to the photocatalytic activity of semiconductors.

As the global landscape is changing with increasing population power source has become principal focus in the scientific field. Energy storage is an alternate in renewable power source field that results in various energy storage devices of different mechanization. Supercapacitors having high energy and power density with good cyclability than batteries potential considered as the best storage systems and more attracted one. Out of four main constituent's electrode material, electrolyte, collector and separator of supercapacitor, electrode material and electrolyte plays an important role. The key issue is the synthesis of electrode material for the supercapacitor's development.

Further the last few eras, nanomaterials contribute significantly in the sensor field development. The essential components of pharmaceuticals are identified in samples from environment and wastewater, contains diverse constituents, such as antibiotics, analgesics, antipyretics, anti-inflammatories, hormones, and antimicrobials. As the results of these contents, accumulation of toxicity level predominates in the eco system, pose sever issues even in trace level, and these are resistant to biological degradation procedures and almost

completely escaped from sewage treatments. Emerging electrochemical detection technique, positioned top in the comparative steps with other methods. High electrical conductance, large surface area, better mechanical strength and high chemical stability are the properties of the electrode promotes movement of electron at electrode interface that motivate the reaction. In this regard, various nanomaterials modified with different form of carbon paste electrode used to identify for various analyte.

The material with suitable band gap can be used as photocatalyst under solar light has to be suitably identified. Along the its characteristics nature suitable for application towards energy devices and sensors has to be recognized. Because as a cost-effective approach multiple application for the nanomaterial were in demand. Among many semiconductors materials metal oxide of spinel structure was identified as prefect for the all applications. Hence based on the literature survey the most suitable material for our research work and recognised by its features was $Bi_2Zr_2O_7$.

The present work aims to synthesize $Bi_2Zr_2O_7$ based material that should be utilized as photocatalyst in photocatalytic degradation with good recycling stability, as a supercapacitor having better energy storage aspects and as sensor material to be used in bio medical field, concisely a multifunctional $Bi_2Zr_2O_7$ and related dopant with composited NPs were focused. Briefly, the aim of our work is to synthesis the $Bi_2Zr_2O_7$ by simple solution combustion method and tune its properties by doping and compositing to improve physical and chemical properties for the multiple fields of applications.

3.0 LITERATURE SURVEY

- A.S.Rajashekharaiah et.al., [43] reoprted the novel $Bi_2Zr_2O_7:Sm^{3+}$ (1–9 mol%) nanoparticles (NPs) were synthesized via sonochemical method using Cetyltrimethylammonium bromide (CTAB) as a surfactant. The effects of primary

synthesis conditions (pH, growth time, surfactant and dopant concentration) on the surface morphology have been reported for the first time. Photoluminescence (PL) studies ($\lambda ex = 465$ nm), CIE and CCT values revealed that the present nanophosphor could meet the needs of illumination devices and also for domestic appliances. Thermoluminescence studies show a well-resolved glow peak observed at ~ 182 °C along with a shoulder peak at ~ 116 °C be a good candidate for radiation dosimetric applications. This gamma dosimeter can be applied in the routine TL Dosimetry badge system among the gamma radiation workers involved in nuclear fuel cycle operations. Photocatalytic performance of at 5 mol% was experimented in the decolorization of Methylene Blue (MB) under natural Sunlight irradiation.

- Venkatesan Jayaraman et. al., [44] reported on a strong redox ability photocatalyst of CdCuS solid solution composited with pyrochlore like $Bi_2Zr_2O_7$ has been fabricated by the simple hydrothermal method. The robust CdCuS solid solution materials perform the supporting role to the $Bi_2Zr_2O_7$ nano materials. The structural, optical, valence and vibrational states of the prepared heterostructure materials were analyzed using various characterization techniques. The photocatalytic activity of the as-synthesized $Bi_2Zr_2O_7$/CdCuS heterostructure has been verified under direct solar light and ambient conditions. The synthesized $Bi_2Zr_2O_7$/CdCuS nano combination exhibits a better photocatalytic activity for the removal of methylene blue and 4-nitrophenol organic probe molecules. The heterostructure formation between the samples is confirmed by HRTEM analysis. The improved rate of the photocatalytic reaction of the samples is attributed to the formation of heterostructures at the interface. The close interfacial contact between the two materials discloses the effective charge transfer, which leads to suppressed charge carrier recombination. The enhanced photo catalytic activity of redox-mediator-free-$Bi_2Zr_2O_7$/CdCuS heterostructure, possibly will be credited to the robust

redox ability and the several charge transfer channels in the tight contact. The chief radicals produced in the catalytic reduction reaction have been predicted by the scavenger trapping methods and the results are discussed in detail. The obtained information from this study on $Bi_2Zr_2O_7$/CdCuS delivers some new visions for the design of active photocatalysts with multiple benefits.

- Yijia Luo et. al., [45] reported the new synthetic route is presented to prepared pure $Bi_2Zr_2O_7$ material, in which a $NaNO_3/KNO_3$ molten salt is used to obtain the resulting $Bi_2Zr_2O_7$ at a relatively low temperature of 400 °C under atmospheric pressure. Powder x-ray diffraction confirmed the structure type and purity of the as-prepared sample, and further revealed that a single-source $Bi(OH)_3.Zr(OH)_4 \cdot nH_2O$ complex precursor plays a crucial role to synthesize $Bi_2Zr_2O_7$ nanocrystals. Scanning electron microscope and transmission electron microscope show the morphologies and sizes of $Bi_2Zr_2O_7$ crystal in detail, and UV–Vis diffuse reflectance measurements evidenced the wide light absorption range. Furthermore, the as-synthesized $Bi_2Zr_2O_7$ with smaller particle size and larger specific surface area exhibit superior photocatalytic activities compared with the sample obtained without adding molten salts.
- Deyong Wu et. al., [46] reported the Bismuth zirconate complex oxides ($Bi_2Zr_2O_7$) with various novel morphologies successfully prepared via a facile sedimentation–calcination method. The structure, morphology, composition and light absorption properties were characterized with X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, high-resolution transmission electron microscopy and UV–vis diffuse reflectance. The photocatalytic activity of $Bi_2Zr_2O_7$ photocatalyst was tested in the reduction of methyl orange under solar light irradiation. The results showed that the prepared sample exhibited irregular morphology with features ranging from 20 to 50 nm in size, had a direct band gap of 2.59 eV and displayed effective photocatalytic activity

under simulated solar irradiation.

- X. Liu et. al., [47] reported, on Tetracycline (TC), an antibiotic, is persistent in nature and frequently detected in water and sediments. Visible-light-driven photocatalyst for TC degradation is a promising environmental-friendly technology. $Bi_2Zr_2O_7$, an effective photocatalyst, but no studies on its photodegradation of TC could be found in literature. In this study, $Bi_2Zr_2O_7$ was synthesized by three soft templated sol-gel methods. Three synthesized $Bi_2Zr_2O_7$ catalysts have different structures, morphologies and band gaps. The $Bi_2Zr_2O_7$ nanoparticles synthesized with citric acid as the template (BZO-3) had a larger specific surface area (30.7 m2/g) and a narrower band gap (2.39 eV), and exhibited a better performance for TC degradation under visible light with an efficiency of up to 81.3%. They also exhibited good stability and reusability in recycled experiments. A reaction mechanism of TC degradation by these photocatalyst was proposed. The enhanced photocatalytic performance was mainly due to photo generated holes of reactive species and TC was mainly degraded on the surface of the photocatalyst. Pathways of TC photodegradation were derived from the result of analyses of the reaction intermediates. In conclusion, $Bi_2Zr_2O_7$ nanoparticles were found effective as photocatalyst for TC photodegradation by visible light.
- Vaishali M.Sharma et .al., [48] reported on $Bi_2Zr_2O_7$ was synthesized via a facile solution combustion method. Two different fuels, urea and tartaric acid were used in the synthesis, which resulted in $Bi_2Zr_2O_7$ crystals with different band gaps and surface areas. The structure has been determined by Rietveld refinement followed by the difference Fourier technique. The compound crystallizes in the space group Fd3m with combining macron. The photocatalytic degradation of two dyes was carried out under solar radiation. $Bi_2Zr_2O_7$ prepared using urea as the fuel exhibits a higher photocatalytic activity than the compound prepared using tartaric acid and comparable activity to that of commercial

Evonik P-25 TiO_2. It is suggested that this is due to the oxygen vacancies occurring in the two cases, the urea based compound has occupancy of 0.216, whereas the tartaric acid based synthesis shows disorder in the oxygen position amounting to a small number of oxygen vacancies.

- Tingting He et. al., [49] reported on Novel visible-light response Ag/AgI/ $Bi_2Zr_2O_7$ composites were successfully prepared firstly by a wet chemical route and subsequently a precipitation-photo reduction process. The SEM and TEM results revealed that a number of Ag/AgI nanoparticles are assembled on the surface of the $Bi_2Zr_2O_7$nanosheets. The HRTEM, DRS and XPS results determined the formation of AgO in the photo reduction process. The visible-light photocatalytic activities of the as-prepared samples were evaluated by the degradation of MO aqueous solution. And the Ag/AgI/$Bi_2Zr_2O_7$ composites exhibited excellent photocatalytic activities, which results from the surface plasmon resonance effects of metallic Ag and the formation of a hetero structure between Ag/AgI and $Bi_2Zr_2O_7$.
- Jyoti Pandey et.al., [50] reported on equimolar concentrations of Zr^{4+} and Bi^{3+} were chelated with ethylenediaminetetraacetic acid ligand with the purpose of using it as a precursor to generate pyrochlore-like $Bi_2Zr_2O_7$. When the X-ray amorphous precursor was calcined at 750 °C for 3 h in air, pyrochlore-like product with superstructure reflections was identified by powder X-ray diffraction (PXRD) along with one minor reflection due to β-Bi_2O_3. This phase was found to be metastable from additional experiments conducted by varying calcination conditions. Structural refinement of PXRD pattern by Le Bail method in $Fd\bar{3}m$ space group yielded cubic lattice constant of 10.8421(27) Å. Flower-petal-like morphology of the sample was evident in its field-emission scanning electron microscopy image and energy-dispersive X-ray analysis performed at various locations of the specimen confirmed nearly equal concentration of

zirconium and bismuth. Six bands at 260, 320, 448, 531, 597, and 828 cm^{-1} were observed for this sample in its Raman spectrum and supported our claim of pyrochlore-like structure. Indexation of bright spots present in selected area electron diffraction pattern and observed distances of lattice fringes in high-resolution transmission electron microscopy image were in conformity with the results from PXRD measurements. Absorbance maxima at 312, 372, and 423 nm with a broad tailing stretching up to visible region was noticed in the UV–visible spectrum of this sample. Direct band gap of 2 eV was estimated for this sample from Tauc plot. The oxygen ion conductivity of the sample in the temperature range of 333–773 K was examined, and the highest conductivity at 773 K was 3.071×10^{-6} S/cm. From activation energy estimation and dielectric loss analysis, thermally activated process related to the mobility of oxygen ion vacancy was found responsible for the observed ionic conductivity. A similar conclusion was reached after careful analysis of dielectric spectroscopy data of this sample. High surface area (125.04 m2/g) and mesoporosity (pore diameter of 3.81 nm) were possessed by this sample, which paved way for studying its catalytic role in the reduction of nitroaromatics and carcinogenic Cr^{6+} Cyclability experiments showed the retainment of catalytic activity up to five cycles by the sample without undergoing any structural change.

- Zhengjun Qu et.al., [51] reported the high re-combination rate of photogenerated carriers and the low redox capability of the photocatalyst are two factors that severely limit the improvement of photocatalytic performance. Herein, a dual Z-scheme photocatalyst bismuthzirconate/graphitic carbon nitride/silver phosphate ($Bi_2Zr_2O_7$/g-C_3N_4/Ag_3PO_4 (BCA) was synthesized using a co-precipitation method, and a dual Z-scheme heterojunction photocatalytic system was established to decrease the high re-combination rate of photogenerated carriers and consequently improve the photocatalytic performance. The re-combination of electron-hole pairs (e- and h+) in the valence band (VB) of g-C_3N_4

increases the redox potential of e- and h+, leading to significant improvements in the redox capability of the photocatalyst and the efficiency of e--h+ separation. As a photosensitizer, Ag_3PO_4 can enhance the visible light absorption capacity of the photocatalyst. The prepared photocatalyst showed strong stability, which was attributed to the efficient suppression of photo-corrosion of Ag_3PO_4 by transferring the e- to the VB of g-C_3N_4. Tetracycline was degraded efficiently by BCA-10% (the BCA with 10 wt.% of 4) under visible light, and the degradation efficiency was up to 86.2%. This study experimentally suggested that the BCA photocatalyst has broad application prospects in removing antibiotic pollution.

4.0 OBJECTIVES OF THE PROPOSED RESEARCH

Our reported research work emphases on $Bi_2Zr_2O_7$ nanomaterial synthesized by solution combustion method using Pudina extract as green fuel.

The main objectives of our thesis work is as follows:

- To synthesis $Bi_2Zr_2O_7$, Ag doped $Bi_2Zr_2O_7$ and Hydroxy hepatite-$Bi_2Zr_2O_7$ composite by rapid, low cost and eco-friendly solution combustion synthesis using pudina extract as a green fuel.
- Characterization of the all the synthesised NPs to be done by P-XRD, SEM-EDAX, HRTEM, FT-IR, XPS and UV-Visible spectroscopy studies.
- The characterisation studies support the size and crystallinity of the nanoparticle by PXRD, morphology by SEM and TEM, Functional groups by FTIR, oxidation state of the metal by XPS were analysed and gives the confirmation of the synthesised nanoparticle.
- The change in chemical and physical property of synthesized samples by doping or by composites formation were identified and analysed in detail.
- The synthesised Nps will be subjected for the photocatalytic dye degradation of selected

organic dyes RhB and MB, under Sunlight irradiation, the mechanism involved in the degradation should be analysed.

- ❖ The electrochemical investigations of synthesized samples will be carried out using CV and EIS techniques at different scan rate using 3-electrode system in 0.1 M KCl aqueous electrolyte.
- ❖ Further, the electrodes will be subjected for sensor application to sense the chemical and Biomolecule toxic substance like lead nitrate and dextrose by electrochemical methods.
- ❖ The antibacterial activity of synthesized samples will be carried out against Gram positive bacterial (*Staphylococcus aureus)* and Gram-negative bacterial (*Salmonella typhi)* and would be discussed in detail.

5.0 METHODOLOGY FOLLOWED

- ➢ The aim of the work is to synthesize $Bi_2Zr_2O_7$ and related nanoparticles by solution combustion method using green as fuel.
- ➢ The synthesized samples are characterized by PXRD, SEM, TEM, EDAX, XPS, FTIR, UV-Visible and subjected to electrochemical, antibacterial and photocatalytic activities.
- ➢ The photocatalytic experiments are carried out at room temperature using circular glass reactor with UV light and Solar light irradiation. The extent of adsorption was found from the equation $Q = (C_0\text{-}C)\ V/W$, where Q is the extent of adsorption, Co and C the concentrations before and after adsorption, V is the volume of reaction mixture and W is the amount of catalyst present in grams.
- ➢ For electrochemical studies, the graphite modified electrode with the synthesised nanoparticle was made and subjected for capacitance and sensor applications.
- ➢ The antibacterial activity of synthesized samples was to be carried out against Gram positive bacterial (*Staphylococcus aureus)* and Gram-negative bacterial (*Salmonella typhi).*

6.0 OUTCOMES OF THE PROPOSED RESEARCH

Nanomaterials are the foundation of nanotechnology and are anticipated to open new paths to numerous emerging technological applications. Nanotechnology is emerging field that covers a wide range of discipline, the design, characterization, production, and application of structures, devices, and systems by controlled manipulation of size and shape at the nanometer scale (atomic, molecular, and macromolecular scale). It is fast advancing into various areas such as biology, chemistry, physics and material science, demonstrating its versatility and playing a vital role in the betterment of the society. It has been predominant advance technology in the synthesis method for the desired nanomaterial targeted for its multitudinous applications reported by the researchers as per literature. The fast development of these nanomaterials lead us for technologically and practically optimistic future. These nanomaterials provides clear view in confronting technological or biological problems that are challenging for mankind. There are countless probabilities to manoeuvre the structural materials to develop devices, only perspective of assembling these miniature has to be improved. This will be helpful to understand and fabricate the novelty of technical devices.

As the final chapter of our present research thesis work is conclusion. The chapter wise systematic conclusion is as follows:

Chapter 1: A concise introduction about BZO nanoparticles, its significance with different method of synthesis and its applications was explained. According to these explanation and literature reports, it mainly focused on significance of synthesis method of our work and its specified combustion method for synthesis of BZO nanoparticles were discussed. Finally, the targeted applications like electrochemical sensor studies, supercapacitor behaviour, biological and photocatalytic activities were also elaborated. The chapter is clinches with objective of our present work.

Chapter 2: To get the BZO nanoparticles of desired shape and size, specific synthetic

technique is important, Accordingly combustion process is employed to synthesis targeted BZO,doped BZO and compsite nanoparticles. The materials and methods utilized for synthesis process were given in detail in chapter 2. The instrumentation explored for characterization of the synthesized material and based on the resulted features the experimental methods for its application procedures are briefly discussed.

Chapter 3: This chapter is focused on synthesis of BZOG and BZOP NP by solution combustion process using glycine as chemical and pudina extract as green fuel respectively. The effect of structure, morphology, optical properties along with the photocatalytic activity were studied for the synthesized NPs. The outstanding performance of BZOP NP due to certain features like lower energy band gap, lower crystallite size with high crystallinity, presence of pores and voids in SEM were the basic reasons for enhanced photocatalytic activity of 97.9% under Sunlight irradiation. The supercapacitor applications and sensing of lead nitrate and dextrose at lower concentration was reported for the very first time for this material which adds an advantage to this paper. The presence of elements in the synthesized sample were confirmed using EDAX and XPS analysis. Finally, it is inferred from the above explanation that BZOP synthesized using green fuel was found to be eco-friendly and also ahead of BZOG in all the aspects which can be utilized for potential practical applications.

Chapter 4: In this chapters, the doping of Ag ions with different concentrations into the host BZOP crystal lattice were discussed in details. BZOP and different mol percentages of Ag-doped BZOP nanomaterials were synthesised by the greener solution combustion method and the synthesised materials were successfully characterised using various spectral, analytical, and electrochemical techniques. 7 mol% of Ag-doped BZOP nanomaterial displayed excellent photodegradation performance against MB (98.7%) and RB (99.3%) dyes due to its distinct properties like semiconducting property, higher binding energy, band gap, optical property, and stability. Using EIS spectral data, it was found that the lowest charge transfer

resistance (Rct-225 Ω) value for 7 mol% of Ag-doped BZOP nanomaterial photocatalyst as compared to BZOP and other mole percentages of Ag-doped nanomaterials. An Ag-doped BZOP-modified electrochemical sensor was used to determine the lead nitrate and dextrose molecules with low detection limit (LOD) values of 18 and 12 μM respectively. Radical scavenging studies revealed that $^{\bullet}O_2^-$ or h^+ reactive species are involved in the photocatalytic degradation of MB and RB dyes under visible light. An enhanced antibacterial activity was observed for Ag-doped BZOP materials as compared to BZOP, which can be attributed to the presence of Ag on the surface of the BZOP lattice for both gram-positive and gram-negative bacteria. Moreover, the Ag-doped BZOP nanomaterial exhibited enhanced stability for the degradation of MB and RB dyes, and the photocatalyst has retained its photodegradation efficiencies even after the fifth cycle. The photocatalytic degradation of dye reactions using Ag-doped BZOP nanomaterials as photocatalysts under visible light irradiation has been discussed.

Chapter 5: In this chapter, the BZO-HA composites are synthesized successfully by simple combustion method and SEM-EDS, FTIR, XRD, electrochemical, and UV-Vis techniques were characterized. The catalyst efficiency is assessed in presence of Sunlight for MB and RB dyes under optimum conditions. The BZO-HA (20%) catalyst is proved to be an efficient one as compared to the Host material. The photogenerated holes, hydroxyl radical, and superoxide anion is responsible for the excellent photocatalytic degradation of MB and RB dyes. In addition, the BZO-HA (20%) composite exhibited better antibacterial activity against E. coli and S. aureus bacteria pathogens owing to the synergistic effect between BZO and HA particles, and the generation of reactive oxygen species. Moreover, the BZO-HA (20%) composite modified electrode showed high selectivity for the determination of dextrose and lead nitrate compounds in 0.1 M KCl as an electrolyte and the applied potential ranging from – 0.8 V to + 1.0 V for 1-5 mM concentration of analytes. Finally, this result

may be a promising route to prepare new semiconductor-based photocatalyst for wide-spectrum of applications.

Chapter 6:

In this chapter, the synthesis of Fe (1-9 mol %) doped bismuth zirconate ($Bi_2Zr_2O_7$) NPs by the green combustion method using *Menthaspicata L.* leaves extract were discussed. The Bragg reflections of the host matrix corresponds cubic pyrochlore-like system. The addition of Fe doped to BZOP host matrix resulted in the growth of other planes of host matrix and also few less intense planes corresponding to monoclinic planes of ZrO_2.. High-resolution XPS spectra of the atoms Bi, Zr, Fe, C and O were examined to learn more about the state of these atoms. The crystallite size was found to increase from 30.4 - 45.8 nm with increase in dopant concentration. However, the energy band gap was found to decrease from 2.33 to 2.09 eV. The photocatalysis, reusability and stability of BZOP:Fe (0-9 mol %) NPs were studied in detail. Due to its high specific capacitance and low charge transfer resistance, BZOP:Fe (5 mol %) can also be employed as a supercapacitor. It acted as a sensor material to detect dextrose and lead metal ion at a very lower concentration of 1–5 mM. BZOP:Fe (5 mol %) NPs exhibited a better antibacterial activity against *S. typhi* and *S.aureus* According to the results of the current investigation, BZOP:Fe (5 mol %) NPs are promising multifunctional material with potential use in biomedicine as a good antibacterial agent, in photocatalysis for degradation of various organic contaminants in wastewater treatment and also as an electrochemical sensor.

7.0 SUMMARY

Conclusively, our present thesis work has scrutinized the efficacious synthesis, characteristic feature and applications of BZOP, Ag doped BZO, Fe doped BZO and BZO-HA composites. It gives the importance of facile, effective low cost synthesis method detail. As well as we

concentrated on reducing the toxic effect of fuel by utilizing green fuel in our experiment. The tuning of physical and chemical properties of BZOP nanoparticles by synthesis method, by doping of metal ions and made it as composites with metal phosphates were well explained in detail. As on application point of view, the resulted properties of BZOP nanoparticles supported for electrochemical sensor studies, supercapacitor nature, biological and photocatalytic activities. Though, the synthesized NPs were explored for limited application, to the best our knowledge the focused BZOP nanoparticles by solution combustion synthesis for the mentioned applications were not reported yet. So this work supports for the sustainable development goals by paved the way to explore vast applications of BZOP nanoparticles both in technological and scientific research that enriches humankind.

Publications

Publications in peer reviewed indexed international journal as First Author: **03**

1) K. Pompapathi, K. S Anantharaju*, K. Nagaraju, B. S. Surendra, S. Meena, B. Uma, S. Malini, Arpita Paul Chowdhury & L. Renuka, Green-engineered synthesis of $Bi_2Zr_2O_7$ NPs: excellent performance on electrochemical sensor and sunlight-driven photocatalytic studies. Environ Sci Pollut Res (2023),1-21, Q1, Impact factor-**5.8,** **https://doi.org/10.1007/s11356-022-24760-5**

2) K. Pompapathi, K. S Anantharaju *, B. S. Surendra, S. Meena, B. Uma, Arpita Paul Chowdhury, H. C. Ananda Murthy, Synergistic effect of a $Bi_2Zr_2O_7$ and hydroxyapatite composite: organic pollutant remediation, antibacterial and electrochemical sensing applications, RSC Adv., 2023, 13, 28198, Q1, Impact factor-**3.9,** **DOI:10.1039/d3ra05222b**

3) K. Pompapathi, K.S Anantharaju *, P. Karuppasamy, S.Meena, B.Uma, B.S.Surendra, Arpita Paul Chowdhury, HC Ananda Murthy, Visible-Light-Driven Mentha spicata L.-Mediated Ag-Doped $Bi_2Zr_2O_7$ Nanocomposite for Enhanced Degradation of Organic Pollutants, Electrochemical Sensing, and Antibacterial Applications, ACS Environ. Au 2024, Q1, Impact factor - **3.3,** **https://doi.org/10.1021/acsenvironau.3c00057**

4) K. Pompapathi, K.S Anantharaju *, P. Karuppasamy, S.Meena, B.Uma, B.S.Surendra, Arpita Paul Chowdhury, HC Ananda Murthy, Mentha spicata L.-Mediated Fe-Doped $Bi_2Zr_2O_7$ Nanocomposite for Enhanced Degradation of Organic Pollutants, Electrochemical Sensing, and Antibacterial Applications, Inorganic Chemistry Communication, [Communicated]

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3. International Conference on "Advanced in Materials, Ceramics and Engineering Science (AMCES - 2020)" held on 13th-15th Mar 2023, Organized by Department of AE, BT, CV, Chem and ME, Dayananda Sagar College of Engineering, Bengaluru, Karnataka.

Proposed content of the thesis (chapters and section titles).

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1.2 Zirconate nanomaterial
1.2.1 Bismuth-Zirconate nanomaterial: $A_2B_2O_7$ Structure
1.3 Significance of Nano-Bismuth-Zirconate in our work
1.4 Synthesis methods
1.5 Significance of synthesis method in present thesis
1.6 General applications of nanomaterials
1.7 Photocatalysis process
1.8 Electrochemical applications
1.8.1 Nature of Supercapacitors
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1.9 Microbial studies
1.10 Objectives of our research work
1.11 Review of Literature
Chapter 2 - Materials and methods
2.1 Experimental work
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2.3 Synthesis methods for host and doped $Bi_2Zr_2O_7$ nanomaterials
2.3.1 Combustion synthesis
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2.3.2 Synthesis of host $Bi_2Zr_2O_7$ NPs
2.3.3 Synthesis of doped BZO with (Ag and Fe metal)
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2.3.5 Preparation of the BZO-HA composite
2.4 Characterization techniques
2.4.1 Powder X-Ray diffraction (PXRD) analysis
2.4.2 Scanning electron microscopy (SEM) analysis
2.4.3 Energy Dispersive X-ray Analysis (EDAX) analysis
2.4.4 Transmission Electron Microscopy (TEM) analysis
2.4.5 X-ray Photoelectron Spectroscopy (XPS) analysis
2.4.6 UV-Visible absorption spectroscopy
2.4.7 Fourier transform infrared spectroscopy (FTIR)
2.5 Application studies
2.5.1 Cyclic Voltammetry analysis
2.5.2 CV experimental system
2.5.3 Electrochemical Impedance Spectroscopy (EIS)
2.5.4 Supercapacitor characteristics
2.5.5 Galvanostatic charge/discharge studies (GCD)
2.5.6 Sensors applications
2.6 Photocatalytic activity

Chapter 3 - A new Mentha spicata engineered synthesis of pyrochlore $Bi_2Zr_2O_7$ NPs: Its excellent performance as electrochemical sensor, supercapacitor potential and Sunlight driven photocatalytic studies

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3.2 Results and discussion

3.2.1 Powder X-ray diffraction Studies

3.2.2 Morphological Studies

3.2.2.1 Scanning Electron Microscopy (SEM) analysis

3.2.2.2 Transmission Electron Microscopy (TEM) analysis

3.2.3 Diffused reflectance spectral (DRS) analysis

3.2.4 Fourier transform infrared (FTIR) spectroscopy

3.2.5 XPS analysis

3.3 Electrochemical studies

3.3.1 Cyclic Voltammetry (CV) analysis

3.3.2 Electrochemical Impedance Spectroscopy (EIS) analysis

3.3.3 Sensor studies of Graphite-BZO NPs electrode

3.4 Photocatalytic activity

3.4.1 Detection of reactive oxidative species (ROS)

3.4.2 Photocatalytic mechanism

3.4.3 Photostability

3.5 Antibacterial activity

Chapter 4 - Investigation of insights into the structural properties of visible light driven Mentha spicata L. mediated Ag doped-$Bi_2Zr_2O_7$ nanomaterial for enhanced degradation of organic pollutants, electrochemical sensing and antibacterial applications

4.1 Introduction

4.2 Results and discussions

4.2.1 Powder X-ray diffraction Studies

4.2.2 Morphological studies

4.2.2.1 Scanning Electron Microscopy (SEM) analysis

4.2.2.2 Transmission Electron Microscopy (TEM) analysis

4.2.2.3 Diffused reflectance spectral (DRS) analysis

4.2.2.4 Fourier transform infrared (FTIR) spectroscopy

4.2.2.5 XPS analysis

4.3 Electrochemical studies

4.3.1 Electrochemical sensing of lead nitrate and dextrose

4.4 Photocatalytic activity

4.4.1 Kinetic study of photocatalytic degradation of MB and RB dyes

4.4.2 Radical scavengers study

4.4.3 Reusability and stability study

4.4.4 Photocatalytic mechanism of dye

4.5 Antibacterial activity

Chapter-5 Mentha spicata L.-Mediated Fe-Doped $Bi_2Zr_2O_7$ Nanocomposite for Enhanced Degradation of Organic Pollutants, Electrochemical Sensing, and Antibacterial Applications

5.1 Introduction

5.2 Results and discussions

5.2.1 Powder X-ray diffraction Studies

5.2.2 Morphological Analysis of BZOP:Fe(0-9 mol %) NMs

5.2.2.1 Surface Morphological Analysis of BZOP:Fe(0-9 mol %) NMs

5.2.2.2 Transmission Electron Microscopic Analysis of BZOP:Fe(5 mol % NMs

5.2.3 XPS analysis of BZOP:Fe (5 mol %) NMs

5.2.4 FTIR spectroscopic analysis of BZOP:Fe(0-9 mol %) NMs

5.2.5 UV-Visible Spectroscopic Analysis of BZOP:Fe (0-9 mol %) NMs

5.3 Photocatalytic studies of BZOP:Fe (0-9 mol %) Nps

5.3.1 Photocatalytic degradation analysis

5.3.2 Reusability and stability studies

5.4 Electrochemical studies

5.4.1 Electrochemical investigation of BZOP:Fe (1-9 mol %) NPs

5.4.2 Electrochemical Impedance Spectral Analysis

5.4.3 Electrochemical detection of Lead and Dextrose Glucose

5.5 Antibacterial Mechanism of BZOP: Fe (0-9 mol) %) NMs

Chapter 6 - Insights into synergistic effect between $Bi_2Zr_2O_7$- hydroxyapatite composite for potential application in organic pollutant removal, for antibacterial activity and for electrochemical sensing

6.1 Introduction

6.2 Results and discussions

6.2.1 Powder X-ray diffraction Studies

6.2.2 Scanning Electron Microscopy (SEM) analysis

6.2.3 Diffused reflectance spectral (DRS) analysis

6.2.4 Fourier transform infrared (FTIR) spectroscopy

6.3 Electrochemical studies

6.3.1 Sensor studies of graphite-BZO-HA composite electrode

6.4 Photocatalytic activity

6.4.1 Proposed Photocatalytic Mechanism

6.5 Antibacterial activity

Summary and Conclusion

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